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14. ABSTRACT
Fuel cells based on proton exchange membranes have the potential to provide the core of all Air Force power production, from air-craft ground support equipment to unmanned aerial vehicle and remote power generation. The objective of our program is to develop nanohybrid proton membranes and new proton conductors, which combine high proton conductivity (especially at high temperature/low relative humidity), low gas permeability and methanol crossover, decreased swelling and mechanical robustness for fuel cell applications. High temperature/low relative humidity operation, although desirable, is currently not possible as high temperature gives rise to water evaporation and decreased conductivity. One of the big challenges facing the scientific community is to engineer a membrane material that fulfills all materials requirements, is inexpensive and endures the aggressive fuel-cell environment for a long period of time. Our initial results suggest that nanostructuring can indeed be exploited to circumvent the trade-offs typically found in conventional (composite) membranes.

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FINAL REPORT

Title: Nanogel Polymer Electrolytes

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Agreement Number: F49620-01-1-0082

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Abstract

Fuel cells based on proton exchange membranes have the potential to provide the core of all Air Force power production, from aircraft ground support equipment to unmanned aerial vehicles and remote power generation. The objective of our program is to develop nanohybrid proton membranes and new proton conductors, which combine high proton conductivity (especially at high temperature/low relative humidity), low gas permeability and methanol crossover, decreased swelling and mechanical robustness for fuel cell applications. High temperature/low relative humidity operation, although desirable, is currently not possible as high temperature gives rise to water evaporation and decreased conductivity.

One of the big challenges facing the scientific community is to engineer a membrane material that fulfills all materials requirements, is inexpensive and endures the aggressive fuel-cell environment for a long period of time. Our initial results suggest that nanostructuring can indeed be exploited to circumvent the trade-offs typically found in conventional (composite) membranes.

Despite the extensive R&D efforts in both new polymers as well as hybrid systems, the ideal material has yet to emerge. By and large hybrid membranes investigated to date tend to be lacking in one or more of the properties required for practical applications including proton conductivity, permeation, swelling or mechanical stability.

We have shown that tough, mechanically robust hybrid membranes can be made by incorporating nanoclay particles into Nafion. The nanohybrids exhibit high proton conductivity and low methanol crossover (a factor of five from neat Nafion). Thus, conductivity, methanol crossover and mechanical stability can all be optimized simultaneously in the nanohybrids. In addition, while the conductivity of Nafion drops precipitously at low relative humidity, the conductivity of the nanohybrids crosses over and outperforms Nafion at RH < 50%. Some recent results show that multilayered nanohybrids can become totally impermeable to methanol.

As part of our effort we have been searching for alternative anhydrous proton conductors for fuel cell applications. While Nafion is the standard in industry its conductivity is water content dependent and decreases at high temperatures or low relative humidity. As part of this effort we have synthesized the *first* polyoxometalate-based *ionic liquid* with high temperature proton conductivity ($\sim 10^{-3}$ S cm^{-1} at 140 $^{\circ}$C) under dry conditions by surface functionalization of the solid heteropolyacid $H_3PW_{12}O_{40}$ with a PEG-containing quaternary ammonium cation through partial proton exchange. The proton conductivity of the molten salt is four orders of magnitude higher than that of the solid analogue under identical conditions.

For comparison, the conductivity of Nafion under similar conditions is much less than 10^{-3} S/cm. Since a humid atmosphere is no longer necessary to maintain conductivity, the ionic liquid superacids offer the potential of developing anhydrous proton conductors with practically zero vapor pressure, high temperature stability and without methanol cross-over losses.

Accomplishments –New Findings
Rationale

Fuel cells are presently under intense development for a variety of power generation applications in response to the critical need for a cleaner energy technology. Different fuel cell technologies have been targeted towards different applications depending on unit size and temperature of operation. High temperature fuel cells are targeted towards high power, high-energy systems in large fixed installations. At the other end are ambient (or near ambient) cells designed for small to medium size power needs and portable or mobile applications. While there remain scientific and technological challenges with both types of fuel cells, low temperature cells present the biggest challenge. In this proposal we focus on low temperature fuel cells ($RT < T_{oper} < 150$ °C).

Low temperature fuel cells based on proton exchange membranes have the potential to become an alternative power source from sensors and hand-held wireless systems to unmanned aerial vehicles and remote power generation. Advantages include significantly reduced weight and emissions, lower preparation time before mobilization, reduced logistics and decreased heat signature.

Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. An integral part of the system is the electrolyte membrane, whose function is to maximize proton mobility in order to increase efficiency, while impending cross-over of the fuels or any contaminants. Additionally, the electrolyte membrane must be robust, maintain rigidity over a broad temperature and humidity range and be stable towards oxidation, reduction and hydrolysis while operating near or above the boiling point of water.

A big challenge facing the scientific community is to engineer an electrolyte material that fulfills all the above requirements, is inexpensive and endures the aggressive fuel-cell environment for a long period of time. With such stringent requirements it is not surprising that most R&D efforts for low temperature fuel cells are based on Nafion or one of its relatives (i.e. a Teflon-based sulfonated polymers). In order to maintain reasonable protonic conductivity, Nafion, however, must remain well hydrated (i.e. must remain "wet"), which limits operation to high relative humidity or low temperature environment.

Because of operating temperature limits current fuel cells operate at 30-40% theoretical efficiency. Higher operating temperatures are desirable because of higher efficiency, increased reaction rates at the electrodes, higher ionic conductivity in the membrane and a mitigation of poisoning effects. However, such temperatures are not currently accessible, as high temperatures give rise to dehydration of the membrane and, thus, decreased conductivity.

In addition, the low physical strength of the polymer limits how thin it can be in practical applications, thus also limiting the membrane conductance. Nafion is also soluble in methanol, so in methanol fuel cells, the fuel must be diluted to only about 5% or below when it reaches the membrane to avoid membrane breakdown. Furthermore, the long-

term stability of Nafion under operating conditions is good, but not sufficient for long-term applications. Finally, methanol can permeate the membrane to react at the cathode (so called "cross-over") without producing electricity and thus lowering the overall efficiency. Methanol crossover contributes to loss of fuel and establishes a mixed potential at the cathode leading to lower overall performance.

Despite the extensive R&D efforts in both new polymers as well as hybrid systems, the ideal material has yet to emerge. Specifically for hybrid membranes an array of inorganics of different composition, particle size and dimensionality has already been used, though *nanostructuring* has not been the driving objective. By and large hybrid membranes investigated to date tend to be lacking in one or more of the properties required for practical applications including proton conductivity, permeation, swelling or mechanical stability.

In addition, despite all the research activity in composite membranes even simple structure/property models have yet to emerge. In the absence of such models progress has remained mostly Edisonian.

Nanostructured Polymer-Inorganic Hybrid Membranes
The essence of nanotechnology is the ability to work at the molecular level to create large structures with fundamentally new molecular organization. Materials with features on the scale of nanometers often have properties different from their macroscale counterparts. Important among nanoscale materials are nanohybrids or nanocomposites, materials in which the constituents are mixed on a nanometer-length scale. They often exhibit properties superior to conventional composites, such as strength, stiffness, thermal and oxidative stability, barrier properties, as well as unique properties like self-extinguishing behavior and tunable biodegradability. Uses for this new class of materials can be found in aerospace, automotive, packaging, electronic and biotechnology applications, to list only a few.

A unique aspect of nanohybrids is the lack of properties *trade-offs*. For the first time, there is an opportunity to design materials without the compromises typically found in conventionally filled polymers and composites.

Why do we anticipate nanostructuring to lead to better membrane performance? Let us use Nafion as an example. Nafion consists of a perfluorinated backbone with side chains containing sulfonate groups. Microscopic phase separation produces clusters or domains of the ionic groups into a percolated sponge-like microstructure filled with water. Hydrated proton (H_3O^+) transport through these channels provides the required ionic conductivity.

Water evaporation from the porous membrane will continue as long as the ambient vapor pressure, p_A, is less than

$$p_A < p_0 \exp\left(-\frac{2V_m \gamma_{LV} \cos(\theta)}{R_g T \alpha}\right)$$

where α is the pore radius, θ the contact angle and T the temperature. From the above equation it is clear that the extent of evaporation can be minimized by minimizing the right-hand side of the equation (i.e. by decreasing the temperature, pore size, and contact angle). Since operation temperature is generally fixed, the temperature cannot be reduced in any meaningful way. However, pore size and contact angle (or hydrophilicity of the pore walls) can be controlled by proper material design. Nanostructuring by incorporating nanoparticles into the membrane has the potential to optimize both of these variables.
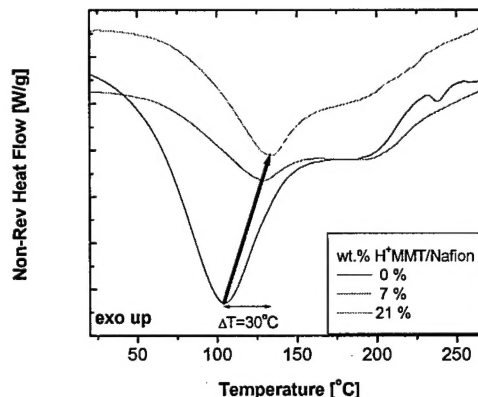
Nafion nanohybrid membranes were prepared by a solvent casting technique as shown below. A liquid phase is used to dissolve the polymer and create a colloidal dispersion of the nanoparticles. Figure 1 presents the different steps that were used to assemble the nanohybrid membranes. Two different dispersion methods were used. The initial membranes were prepared using a mixture of propanol/water to dissolve the polymer and disperse the layered silicates. The second method involved an exchange of the initial solvent of Nafion (propanol/water) for water to dissolve the polymer and create a water based colloidal dispersion. The exchange to water as the dispersion medium created a more stable colloidal dispersion for the nanoparticles, which in turn influenced their dispersability.
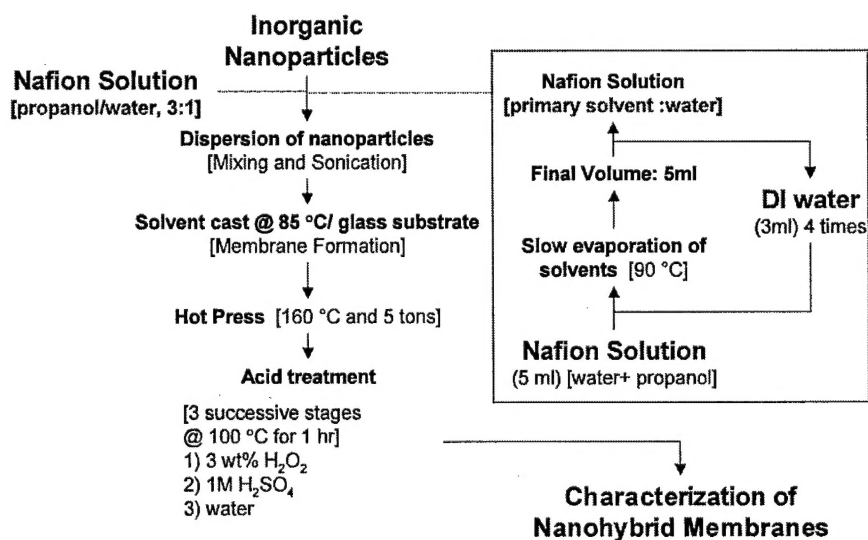
**Schematic showing all the steps for synthesizing nanohybrid membranes**
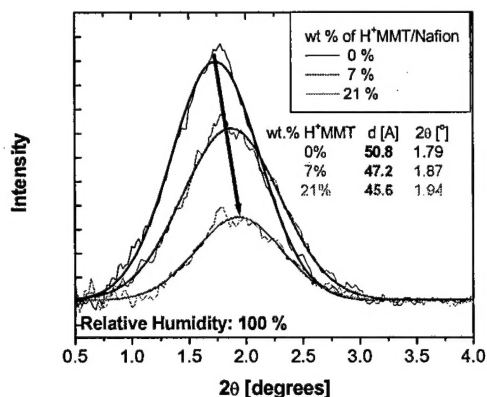
Figure 1. SAXS of Nafion-Nanohybrid membranes. Influence of H⁺MMT on nanostructure of polymer matrix.
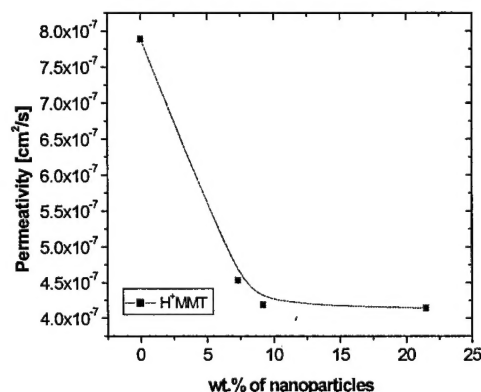

Figure 2. MDSC of Nafion-Nanohybrid membranes. Water retention of polymer matrix with H⁺MMT nanoparticles.

Our results with nanohybrid membranes support the reasoning about nanostructuring outlined above. Incorporation of nanoparticles such as nanoclay into Nafion appears to promote the formation of smaller pores (i.e. domains of hydrated ionic groups) as evidenced by a continuous decrease in cluster size with increasing nanoparticle content seen by Small Angle X-ray Scattering (Fig. 1). For Nafion the mean size of the ionomer clusters is 51 and it decreases to 46 Å for the nanohybrid containing 21wt% of nanoparticles. The combination of smaller pores or channels as well as the hydrophilic nature of the nanoparticles translates into better retention of water (Fig. 2). The DSC traces of the neat Nafion and the nanohybrids show a trend towards higher evaporation temperatures as the amount of the nanoparticles increases. For Nafion the first order transition peak related to the evaporation of water, seen in the non-reversible heat flow, is located at 100 °C. For the nanohybrid membranes, this peak is seen to shift by about 30 °C.
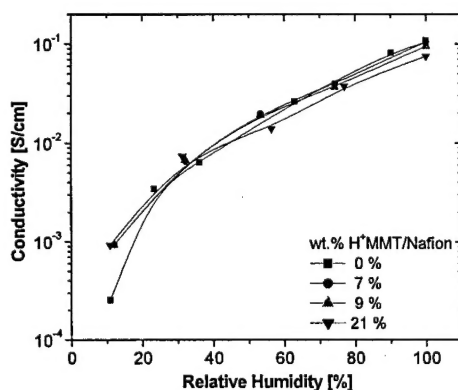
Figure 3. Protonic conductivity of Nafion-nanohybrid membranes showing a crossover at low RH for the nanohybrids.

Figure 4. Methanol permeability of Nafion-Nanohybrid membranes showing a substantial decrease of MeOH permeability in the nanohybrids.

Conductivity measurements under controlled relative humidity, RH, show that, in contrast to Nafion, whose conductivity drops significantly, the nanohybrids retain their conductivity and become more conductive than neat Nafion at low RH (Fig. 3). In addition, the permeability of methanol is decreased in the nanohybrids by a factor of two to five depending on the type of nanoparticles compared to the neat Nafion. (Figure 4). For polymer membranes used in direct methanol fuel cells a critical issue is the methanol permeability from the anode to the cathode. MeOH that crosses over the membrane is wasted lowering efficiency. Thus, conductivity, methanol crossover and mechanical stability can all be optimized simultaneously in the nanohybrids.

In collaboration with MTI Microfuel Cells we have initiated testing of fuel cells based on nanohybrids membranes. While these are preliminary tests, the nanohybrids outperform Nafion membranes. For example, using the product of current at open circuit voltage multiplied by the cell resistance as a figure of merit the fuel cells based on nanohybrids show an improvement of ~30% over pure Nafion at similar conditions.
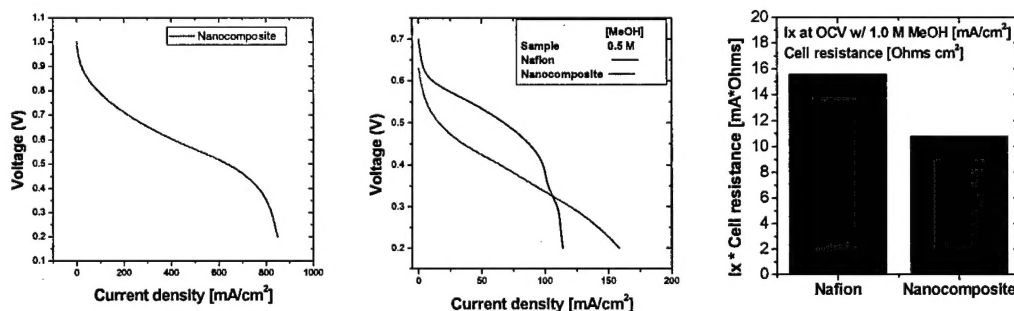

Figure 5. IV curves for Nafion-Nanohybrid membranes with H_2 and MeOH as fuel.

Anhydrous Proton Conductors based on Polyoxometallate Ionic Liquids
In parallel to our work on nanohybrids, we have been searching for alternative anhydrous proton conductors for fuel cell applications. The following describes a new family of polyoxometallate (POM) based liquid salts. The *liquid* POM derivatives are obtained by partial exchange of the surface protons of the POM core cluster by a bulky PEG-containing a quaternary ammonium cation. The POM proton form can undergo partial proton exchange with monovalent ions leading to species with the general formula $H_{3-x}M_xPOM$ (M: monovalent cation, x: degree of proton substitution). Due to the remaining protons, the partially exchanged POMs are well known for their acidic properties. Liquid POM salts offer several advantages: i) they are low vapor pressure liquids; ii) they possess residual acidity and good thermal stability; and iii) they exhibit much higher ionic conductivity than the corresponding anhydrous solid analogues. As such they can find applications in homogeneous catalysis and fuel cell applications.

The ionic conductivity measured by impedance spectroscopy as a function of temperature is shown in Fig. 6. The conductivity follows a Vogel-Tammann-Fulcher (VTF) behavior throughout the temperature range with a conductivity of $6x10^{-4}$ S cm^{-1} at 140 °C. We suspect that the main contribution to the conductivity is the smaller, more mobile protons, compared to the bulky POM clusters and quaternary ammonium counter cations. In comparison, a partially-exchanged POM solid (e.g. K$^+$ derivative) with the same number of protons exhibits much lower conductivity under anhydrous conditions. The temperature dependence of the solid analog is also Arrhenius-like rather than the VTF behavior observed for the liquid derivative.
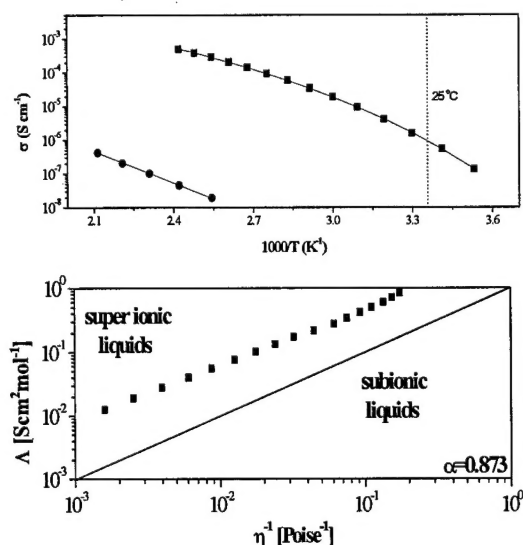

Fig. 6 Top: Ionic conductivity of the POM liquid salt (■) and of a potassium-exchanged POM solid (●) as a function of temperature. Bottom: Walden plot of POM liquid salt.

One way of assessing the ionicity of ionic liquids is based on the classical Walden rule ($\Lambda\eta$= constant) that relates the ionic mobility, represented by the equivalent conductivity Λ to the fluidity $\phi=\eta^{-1}$. For ideal ionic solutions (i.e. fully dissociated ions of equal mobility) the ideal behavior lies on the diagonal of Fig. 6, bottom. Behavior below the diagonal indicates that there is a high degree of correlation between cations and anions (e.g. ion-pairing) so that the conductivity is less than expected for certain fluidity. In contrast, behavior that lies above the diagonal is characterized as superionic and is associated with conduction mechanims that are more efficient than the Walden mechanism. Superionic slip of small ions in some melts and the Grothhus mechanism for certain protonic solutions are an example of such behavior. Recently Angell and coworkers have shown that these arguments can be extended to ionic liquids.

The behavior for the POM liquid derivative falls above the diagonal suggesting that ion movement is characterized by a mechanism that is more efficient than the Walden ideal behavior. While we are yet to identify the conduction mechanism it is clear that the

conductivity is higher than that expected from the corresponding fluidity. The slope on the conductivity vs fluidity plot is about 0.9 suggesting that the ion relaxation modes are highly coupled to the matrix modes.

Finally, while the connection between high conductivity and vapor pressure is not obvious, Angell and coworkers have suggested that both depend on the formation of an "ideal" quasi-lattice. The more uncorrelated the motion of the cations and the anions, the higher the conductivity but also the larger the Madelung energy of the liquid, hence the larger the energy that is required to remove an ion pair into the vapor phase resulting into a lower vapor pressure. Based on Fig. 6, bottom, we suggest that the POM liquid derivative exhibits a low vapor pressure, which is beneficial for high temperature fuel cell and catalytic applications.

Personnel Supported.

Rafael Herrera (graduate student)

Kanan Raman (visiting scientist)

Publications

1. M.M.M. Muthu, E. Hackett and E.P. Giannelis, "From Nanocomposite to Nanogel Polymer Electrolytes", Journal of Materials Chemistry, 13, 1, **2003**.

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4. S. Cypes, W.M. Saltzman and E.P. Giannelis, "Organosilicate-Polymer Drug Delivery Systems: Controlled Release and Enhanced Mechanical Properties", Journal of Controlled Release, 90, 163, **2003**.

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8. J-H. Chang, Y. U. An, S.C. Ryu and E.P. Giannelis, "Synthesis of Poly(butylenes terephthalate) Nanocomposites by In-situ Interlayer Polymerization and Characterization of its Fiber", Polymer Bulletin, 51, 69, **2003**.

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11. K.M. Tyner, M.S. Roberson, K.A. Berghorn, L. Li, R.F. Gilmour Jr., and E.P. Giannelis, "Intercalation, Delivery, and Expression of the Gene Encoding Green Fluorescence Protein Utilizing Nanobiohybrids", Journal of Controlled Release, xx, 00, **2004**.

12. D. Shah, P. Maiti, E. Gunn, D.F. Schmidt, D.D. Jiang, C.A. Batt and E.P.

Giannelis, "Dramatic Enhancements in Toughness of Polyvinylidene Fluoride Nanocomposites via Nanoclay-Directed Crystal Structure and Morphology", Advanced Materials, 16, 1173, **2004**.

13. D. Shah, P. Maiti, D.D. Jiang, C.A. Batt and E.P. Giannelis, "Effect of Nanoparticle Mobility on Toughness of Polymer Nanocomposites", Advanced Materials, in press.

14. A. B. Bourlinos, R. Herrera, N. Chalkias, D. D. Jiang, Q. Zhang, L. A. Archer, and E. P. Giannelis, "Solvent-Free Functionalized Nanoparticles with Liquid-like Behavior", Advanced Materials, in press.

15. A. B. Bourlinos, S.R. Chowdhury, D. D. Jiang, Y-U. An, Q. Zhang, L. A. Archer, and E. P. Giannelis, "Layered Organosilicate Nanoparticles with Liquid-like Behavior", Small, in press.

Invited Talks to Conferences, Seminars
    175. ACS, Colloid & Surface Chemistry, New York, NY (September 2003)
    176. ACS, Polymer Chemistry & Nanotechnology, New York, NY (September 2003)
    177. IEEC Symp. on Emerging Technologies in Packaging, Binghampton, NY (Sept. 2003)
    178. ACS Rubber Division, Cleveland, OH (October 2003)
    179. Functional Fillers –Workshop on Nanocomposites, Atlanta, GA (October 2003)
    180. Workshop in Drug Delivery, Ithaca, NY (October 2003)
    181. 1st World Congress on Nanocomposites, San Francisco, CA (November 2003)
    182. Symposium on Nanostructured Polymeric Materials, Strasbourg, France (March 2004)
    183. IPC, Opportunities in Disruptive Technologies, Baltimore (May 2004)
    184. 11th European Conference on Composite Materials, Rhodes, Greece (May 2004)
    185. PPS-20, Akron, OH (June 2004)

Invited Seminars to Industry
    123. Rhodia, Paris, France, (September 2003)
    124. Rohm and Haas, Springfield, PA (October 2003)
    125. Bayer, Pittsburg, PA (November 2003)
    126. Atofina, King of Prussia, PA (December 2003)
    127. OilDri Corporation, Lincolnshire, IL (March 2004)
    128. Saint-Gobain Innovation Day on Nanomaterials, Northboro, MA (May 2004)
    129. Pactiv, Canandaigua, NY (June 2004)
    130. UOP, Des Plaines, IL (June 2004)

Interactions/Transitions

We are collaborating with MTI Microfuel Cells, who have expertise in testing of fuel cells to further evaluate the nanohybrid membranes. We are also collaborating with UOP a maker of zeolitic and other types of nanoparticles.

New discoveries, inventions, or patent disclosures.
1. J. Zhu, B. Park and E.P. Giannelis, "Composite of High Melting Polymer and Nanoclay with Enhanced Properties"

2. A.B. Bourlinos and E.P. Giannelis, "Functionalized Nanostructures with Liquid-like Bahavior".

Honors/Awards
EPG, Member of Editorial Board, *Small*, Wiley-VCH